Understanding Electrode Interface Through Cryogenic Electron Microscopy

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BATTERY 500 CONSORTIUM

Project ID: bat361

Overview

Timeline

- Start: Oct 1, 2016
- End: Sep 30, 2021
- Percent complete: 70%

Budget

- Total project funding $50,000k from DOE
- Funding for FY19 $10,000k
- Funding for FY20 $10,000k

Barriers

Barriers of batteries

- High cost (A)
- Low energy density (C)
- Short battery life (E)

Targets: cost-effective and high-energy electrode materials and batteries

Partners

- Collaboration
  - Battery 500 PI's
  - BMR program PI' s
  - Stanford: Prof. Zhenan Bao, Prof. Jian Qin, Prof. Steve Chu, Prof. Wah Chiu, Prof. Robert Sinclair, Prof. Paul McIntyre

Project Objective and Relevance

- Develop lithium-metal based full batteries with 500 Wh/kg specific energy to power electric vehicle and decrease the high cost of batteries.

- Design and fabricate Li metal anodes with high capacity, high coulombic efficiency and long cycle life.

- Screen electrolyte and additives for stable anodes and cathodes.

Milestones

FY19
Q1, Test new Li architectures using B500 protocols (completed)
Q2, Implement polymer or composite films to demonstrate 20% cycle life improvement with thin lithium (50 um) (completed)
Q3, Test thin Cu composites current collector using single layer pouch cells (completed)
Q4 , Quantifying inactive Li using procedures and recipes used by B500 tasks (completed)

FY20
Q1, Quantifying inactive Li using B500 electrolytes and protocols (completed)
Q2, Develop new 3D anode structures and test such using coin cell standard protocols to achieve 300-350 Wh/kg (cell-level) for 200 cycles (completed)
Q3, Develop new polymer protective layers for Li anode, test and report such using coin cell standard protocols (in progress)
Q4, Select 3D Li architectures and polymer protective layers for pouch cells (single layer and multilayers) (in progress)

Approach

Cell design, fabrication and validation

1) Establish cell parameters and requirements for coin cells and pouch cells
2) Integrate nanostructured materials in full cells

3D Li metal host anode and interfacial modification

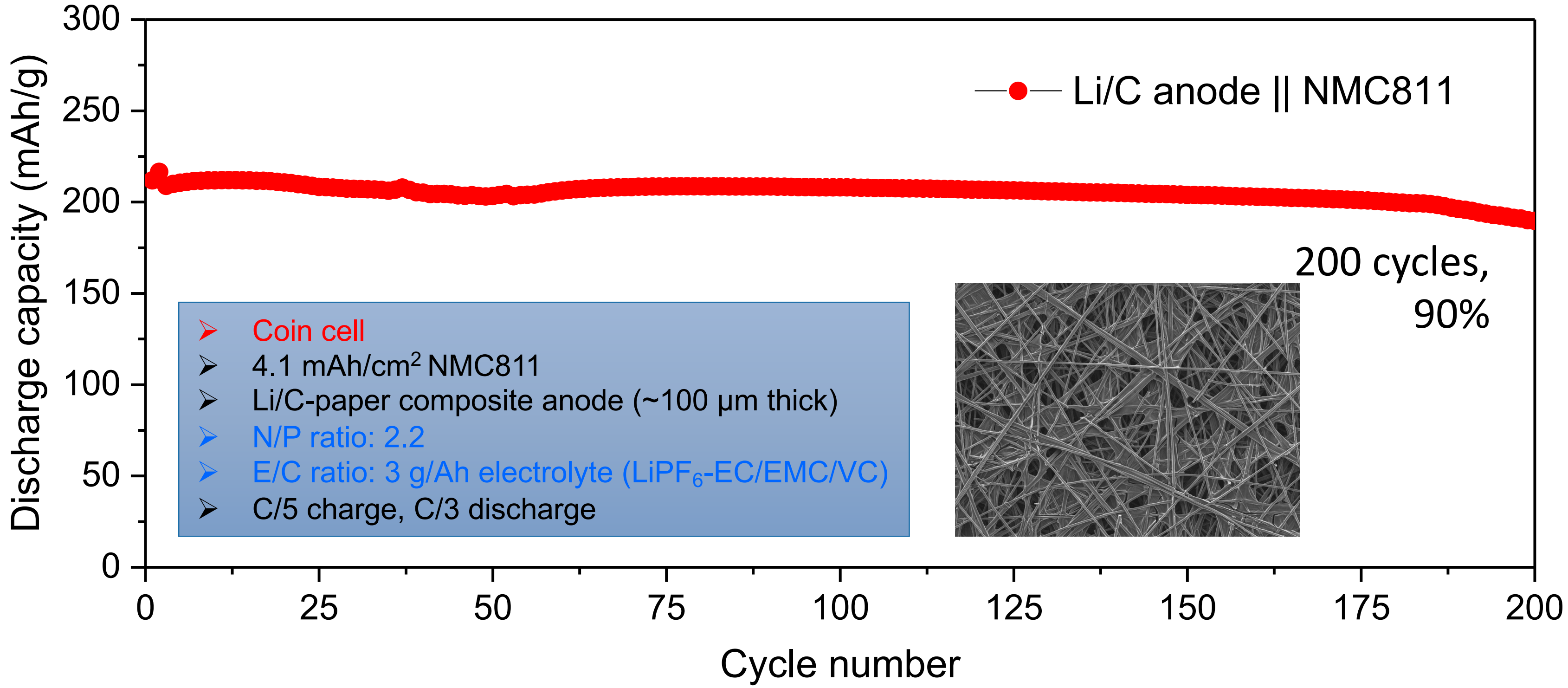
1) Design and synthesize Li metal with 3D host composite to overcome volume expansion and contraction problems.
2) Design surface modification techniques to generate stable interphase by gas phase reaction and advanced polymer coatings
3) Screen electrolytes which can generate stable interface.

Structure and property characterization

1) Transmission electron microscopy
2) Cryogenic electron microscopy
3) In operando X-ray diffraction and transmission X-ray microscopy

Technical Accomplishments and Progress

#1 Long cycling of coin cells with 3D anode (3D carbon nanofiber) that meets the pouch cell requirements for 300 to 350 Wh/kg (332 Wh/kg here)

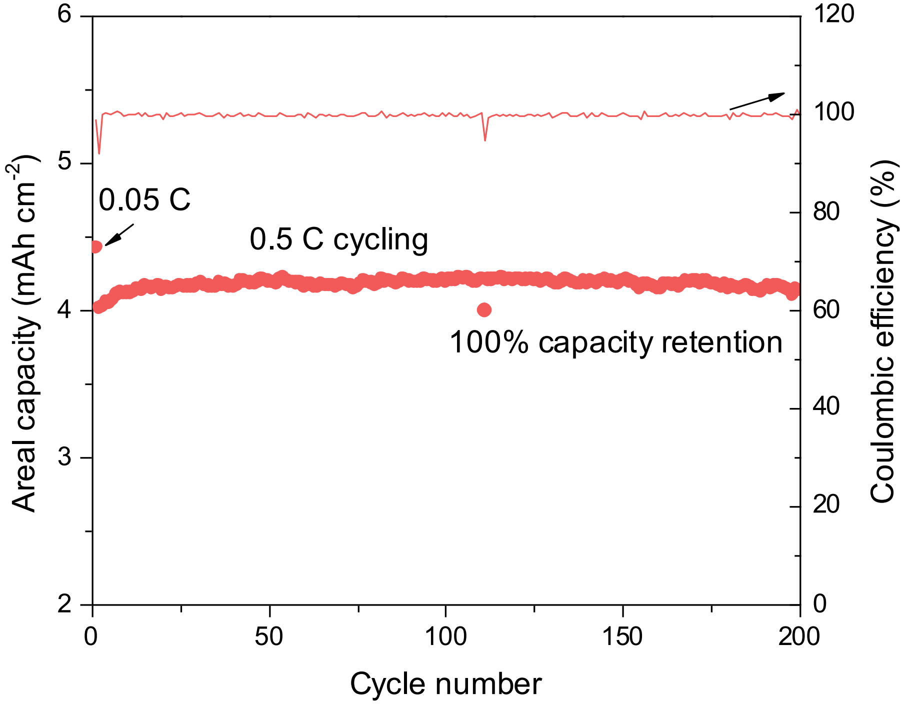


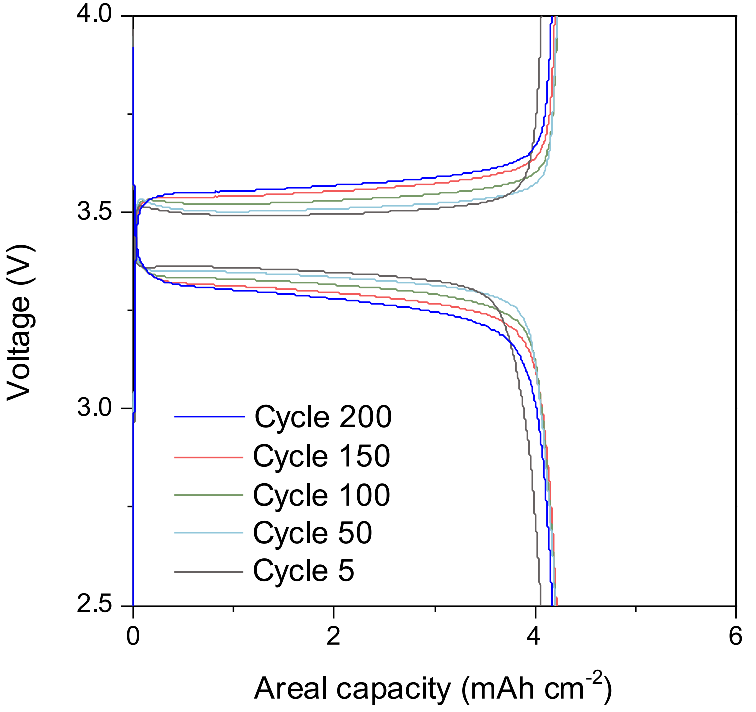
FY20 Q2 milestone, "Demonstrate coin cells with 3D anode structure at 300-350 Wh/kg for 200 cycles."

Work performed by Chaojiang Niu, PNNL.

Technical Accomplishments and Progress

#2: 20 µm Li-rGO||LFP cell



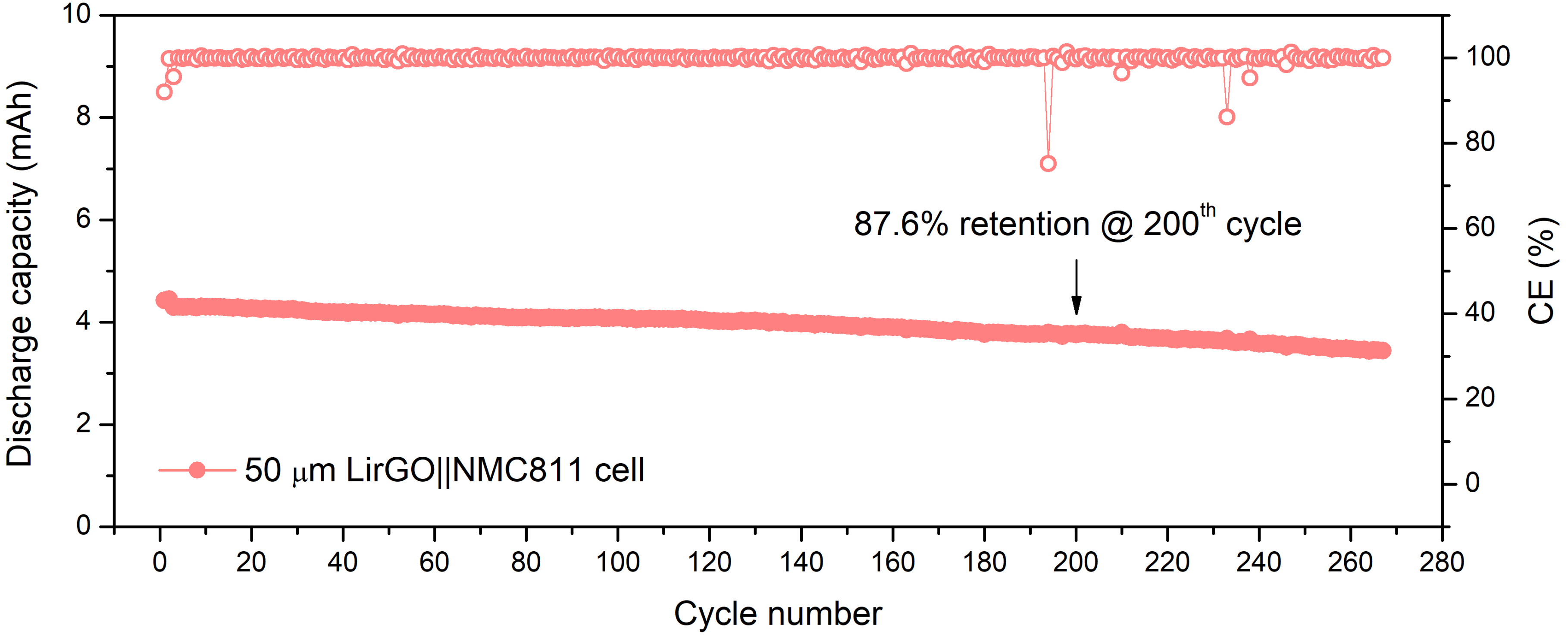


Electrolyte: 6 g/Ah LP40 with 10% FEC and 1% VC additive
Cathode : LFP 4.5 mAh/cm^2
Anode: 20 µm thick Li@rGO host (~ 4 mAh/cm^2)
Cycling: 0.05 C activation, 0.5 C cycling, 2.5~4V

Work performed by Hao Chen and Hansen Wang, Stanford

Technical Accomplishments and Progress

#3: 50 µm Li-rGO||NMC811 cell



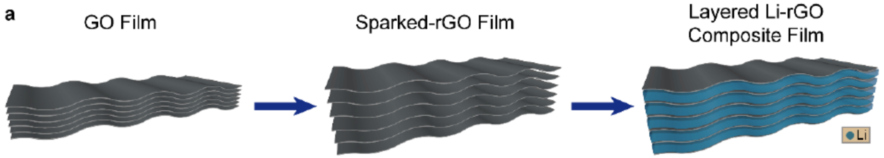
Electrolyte: 3 g/Ah M47 electrolyte (PNNL)
Cathode : NMC811 (commercial from Targary) ~4.2 mAh/cm^2
Anode: 50 µm thick Li@rGO host (~ 10 mAh/cm^2)
Cycling: 0.1 C activation, 0.2 C charging, C/3 discharging, 2.8~4.4V

Work performed by Hao Chen and Hansen Wang, Stanford

Technical Accomplishments and Progress
Li Metal Anode Research Program at Stanford/SLAC

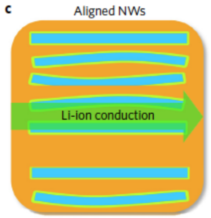
Stable Host

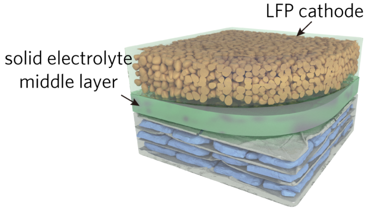
Nature Nanotech. 11, 626 (2016)
Nature Commun. 7, 10992 (2016)
Nature Energy 1, 16010 (2016)
PNAS 113, 2862 (2016)
Nano Lett. 17, 3731 (2017)
PNAS 114, 18 4613 (2017)
Sci. Adv. 3(9), e1701301 (2017)



Solid-state electrolyte

Nano Letters 15, 2740, 2015.
Nano Letters 16, 459 (2016).
Nature Energy 2, 17035 (2017).
Science Advances , 3, eaao0713 (2017).
Nature Nanotech (2019, in press)

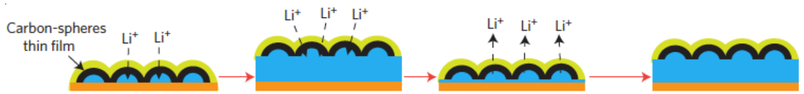




Solid-state Li-rGO/LFP cell

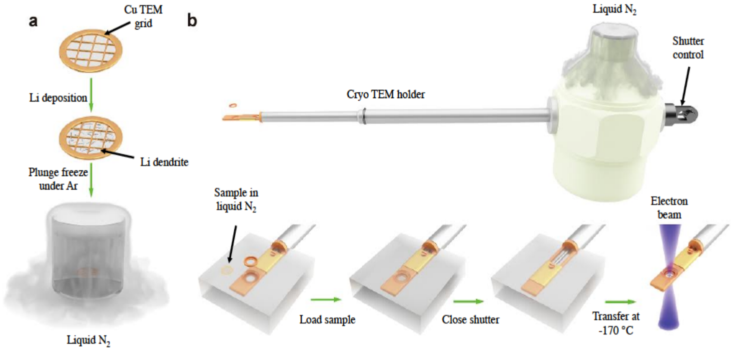
Stable Interface

Nature Nanotechnology 9, 618 (2014).
Nano Letters 14, 6016 (2014).
Nature Communication 6:7436 (2015)
Nature Communication 9:3656 (2018)



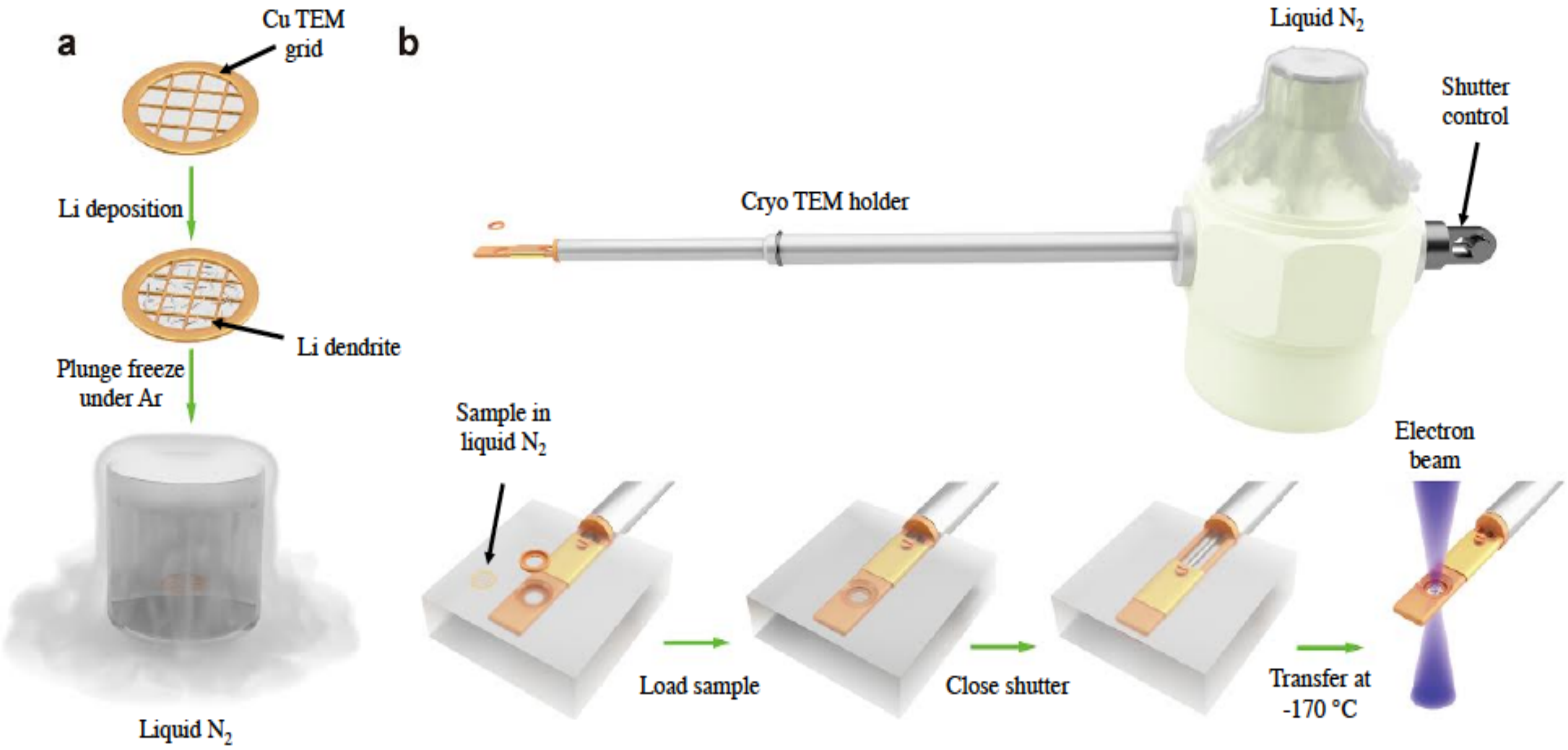
Materials characterizations

Science **358**, 506 (2017)
PNAS, **114**, 12138 (2017)
Nano Lett. **17**, 5171 (2017)



Technical Accomplishments and Progress

Cryogenic Electron Microscopy for Battery Materials



BATTERIES

Atomic structure of sensitive battery materials and interfaces revealed by cryo-electron microscopy

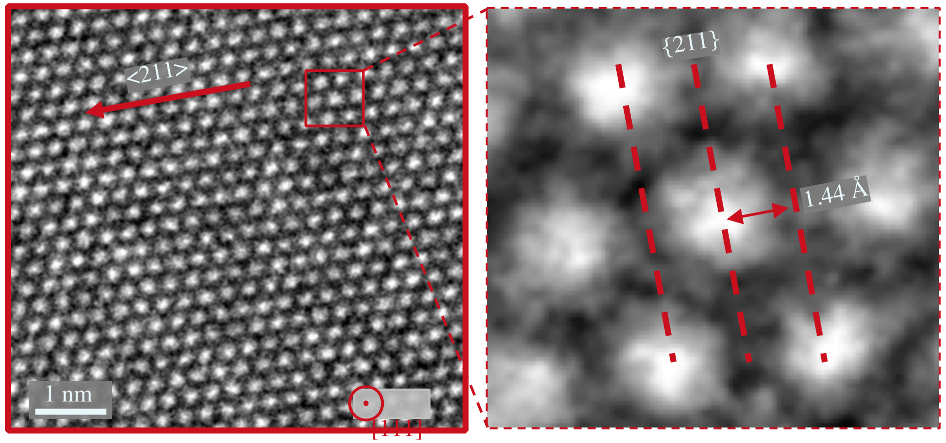
Yuzhang Li,[1*] Yanbin Li,[1*] Allen Pei,[1] Kai Yan,[1] Yongming Sun,[1] Chun-Lan Wu,[1] Lydia-Marie Joubert,[2] Richard Chin,[3] Ai Leen Koh,[3] Yi Yu,[4] John Perrino,[2] Benjamin Butz,[1,5] Steven Chu,[6,7] Yi Cui[1,8]†

15 December 2016; accepted 14 September 2017
10.1126/science.aam6014

Yuzhang Li, Yanbin Li, Yi Cui *Science* 358, 506, 2017.

Technical Accomplishments and Progress

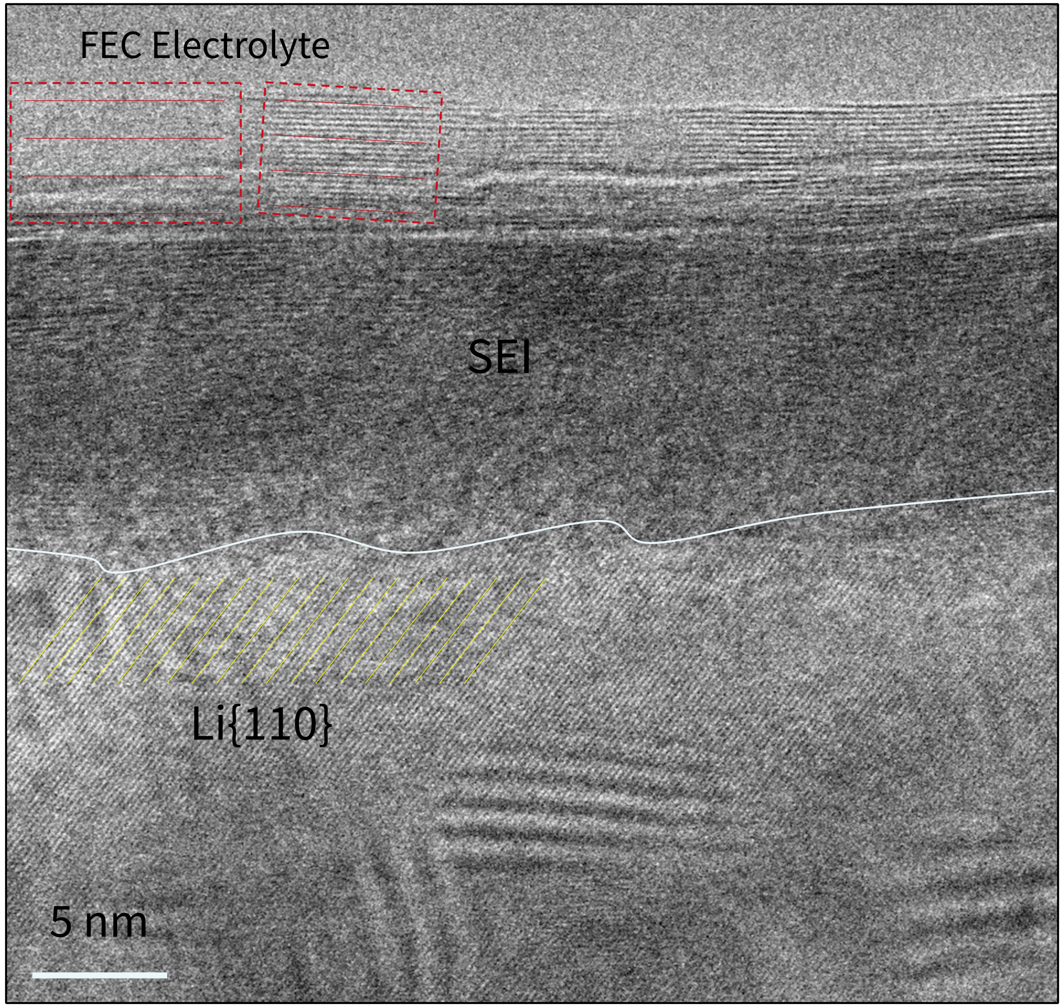
Individual Li metal atoms can be resolved by Cryo-EM



dose rate ~1000 e Å–2 s–1
for ~30 s.

Also see others' CryoEM works on batteries
Shirley Meng (UCSD)
Lena Kourkoutis (Cornell)

First atomically-resolved SEI structure



Yuzhang Li, Yanbin Li, Yi Cui *Science* 358, 506, 2017.

Questions to be answered about SEI

1) How does SEI structure depends on electrolyte composition?

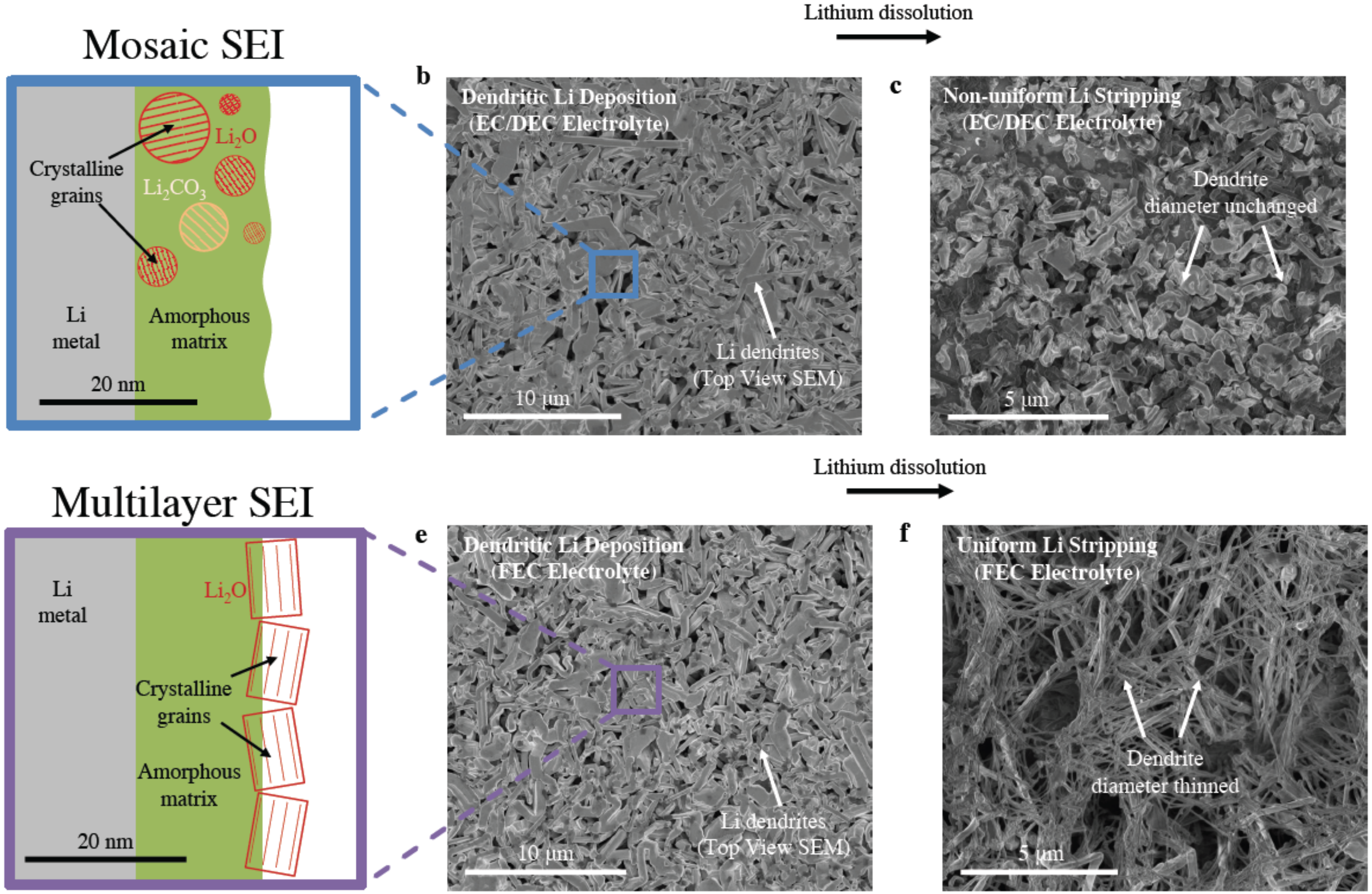
2) How does SEI structure correlate with cycling efficiency?

3) How does SEI structure depends on potential?

4) How does SEI structure depends on temperature?

5) What is the best SEI?

Technical Accomplishments and Progress

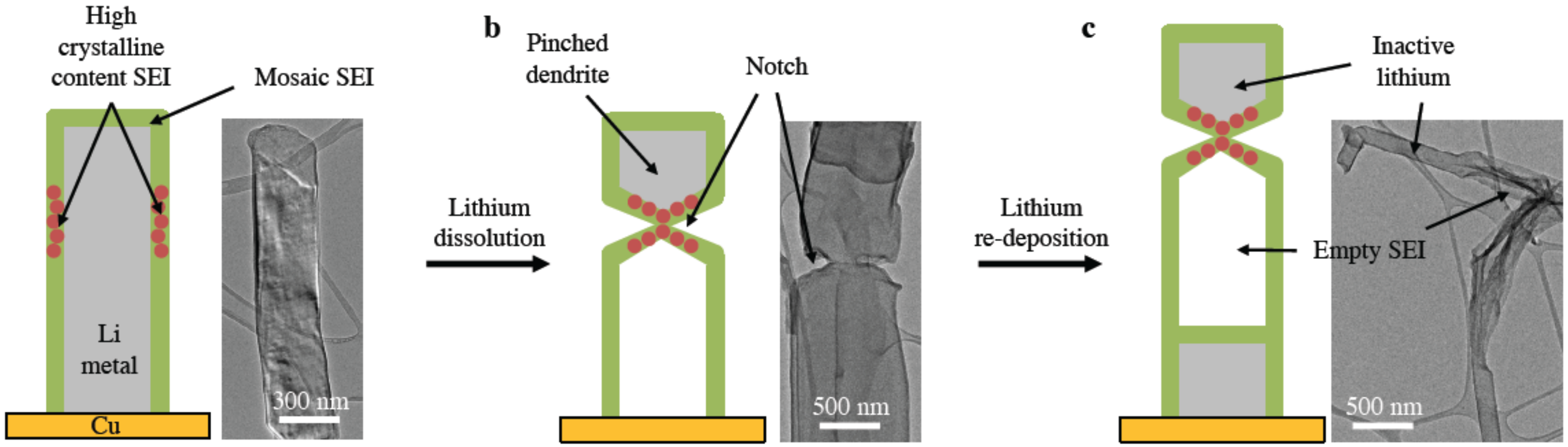


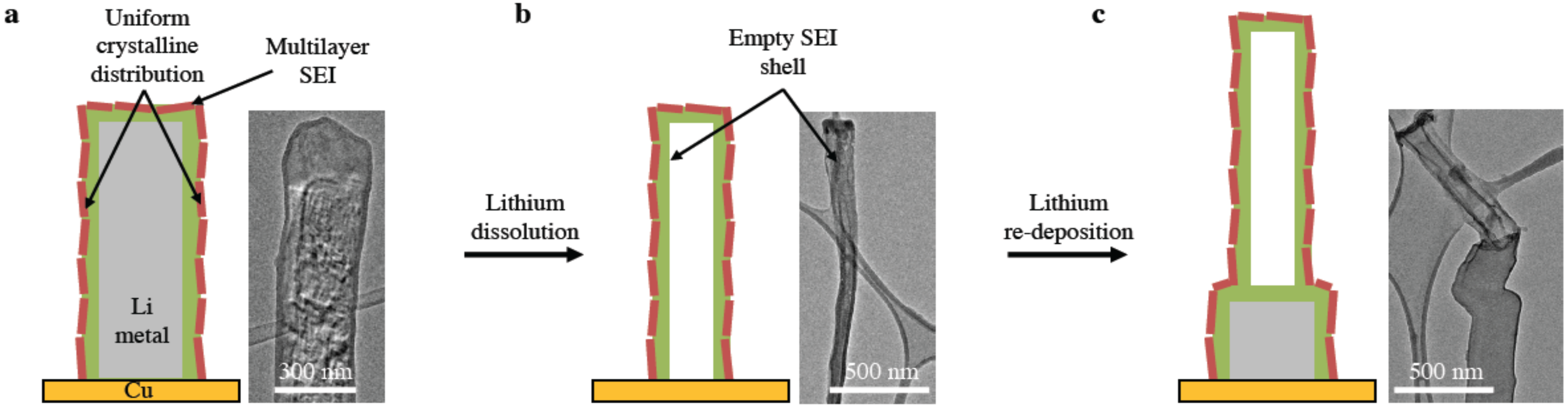
Yuzhang Li, William Huang, Yanbin Li, Allen Pei, and Yi Cui *Joule* (2018, 2,1-11)

Technical Accomplishments and Progress

80% Coulombic efficiency without FEC additive

Cryo-EM Images





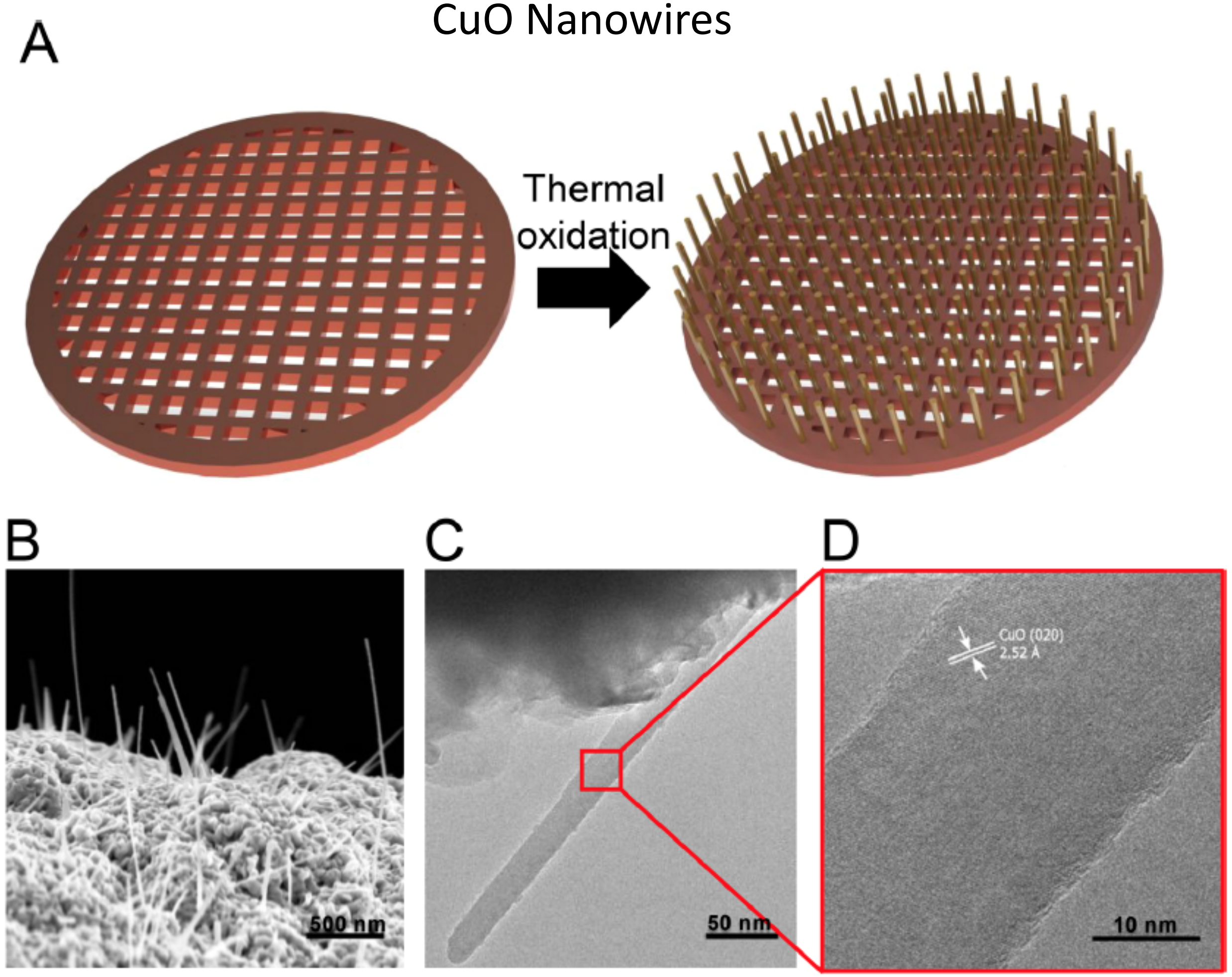
95% Coulombic efficiency with FEC additive

Yuzhang Li, William Huang, Yanbin Li, Allen Pei, and Yi Cui *Joule* (2018, 2,1-11)

Technical Accomplishments and Progress

How does SEI evolve with potential?

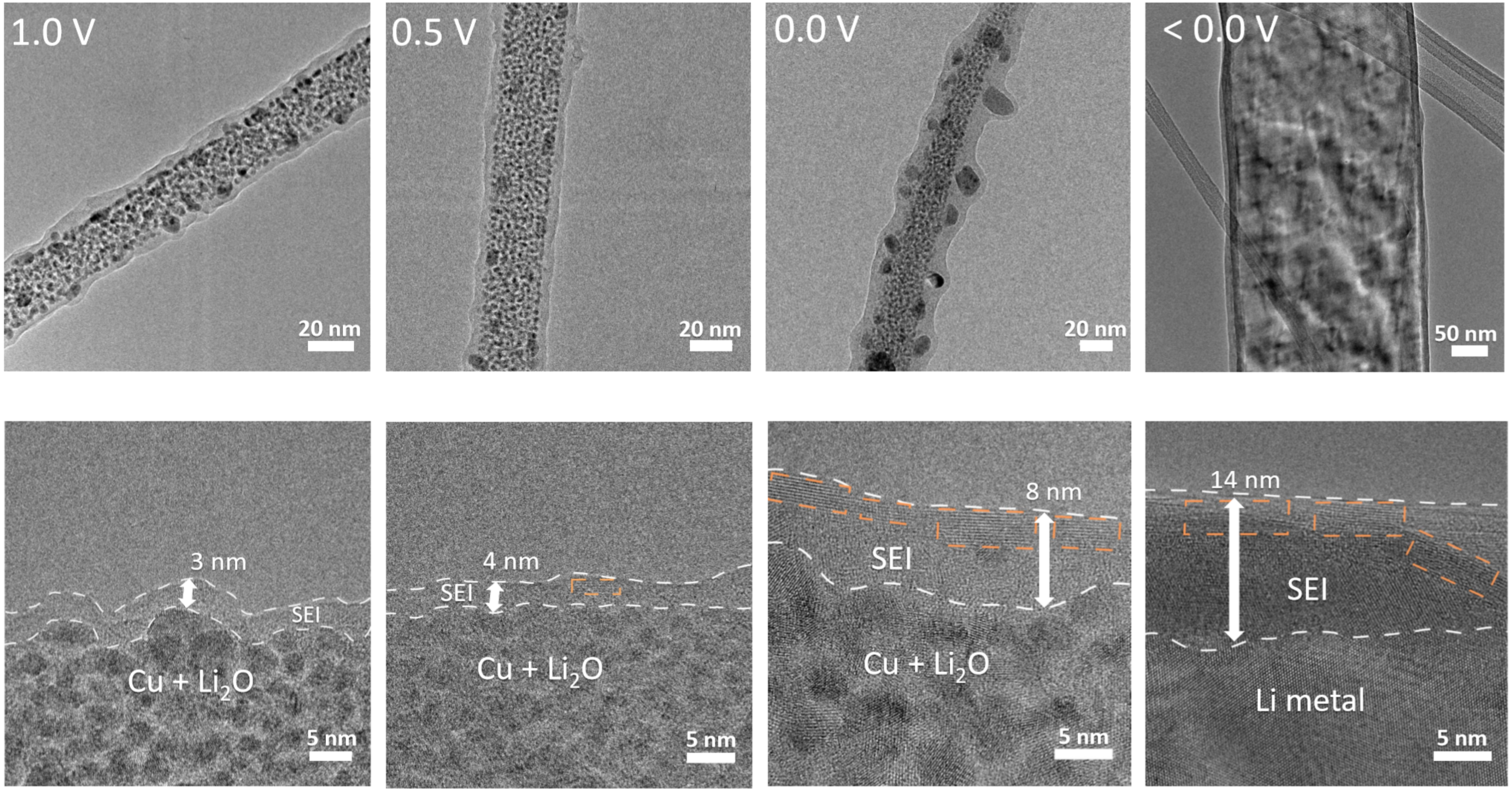
CuO Nanowires



William Huang, David Boyle, Yi Cui, *ACS Nano* 13 , pp 737–744, 2019.

Technical Accomplishments and Progress

SEI nanostructure emerges at low potential



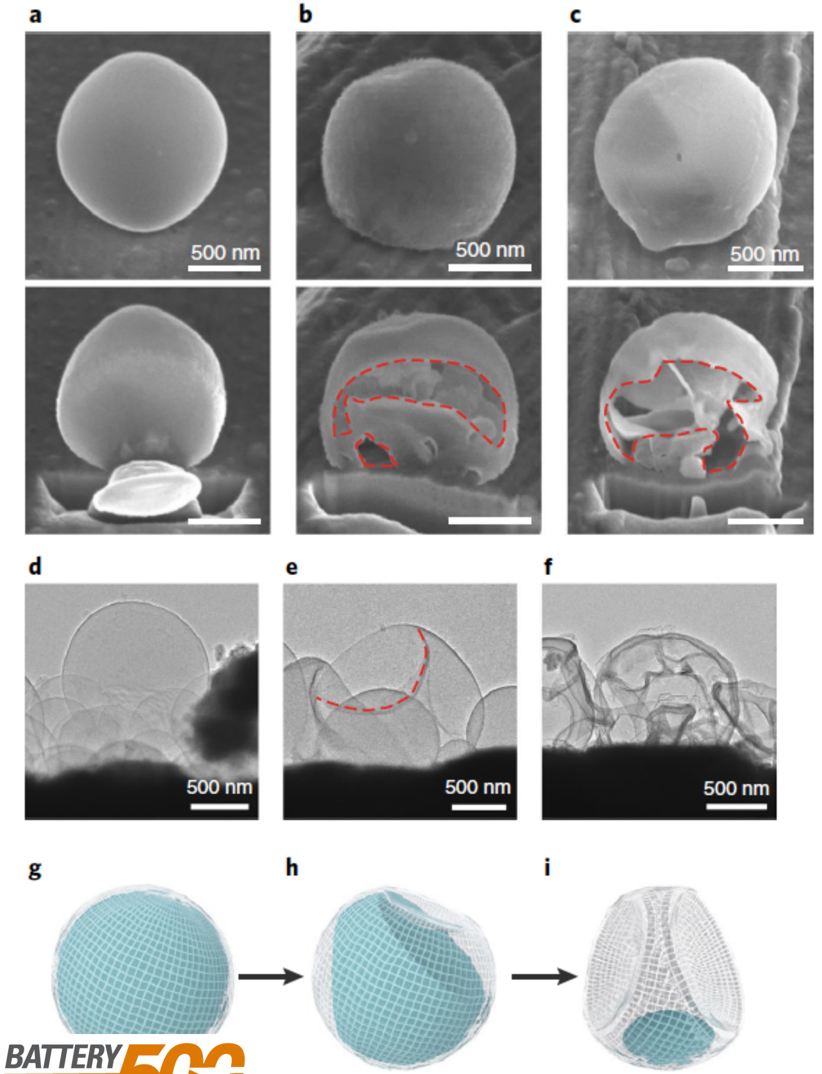
EC/DEC + 10% FEC

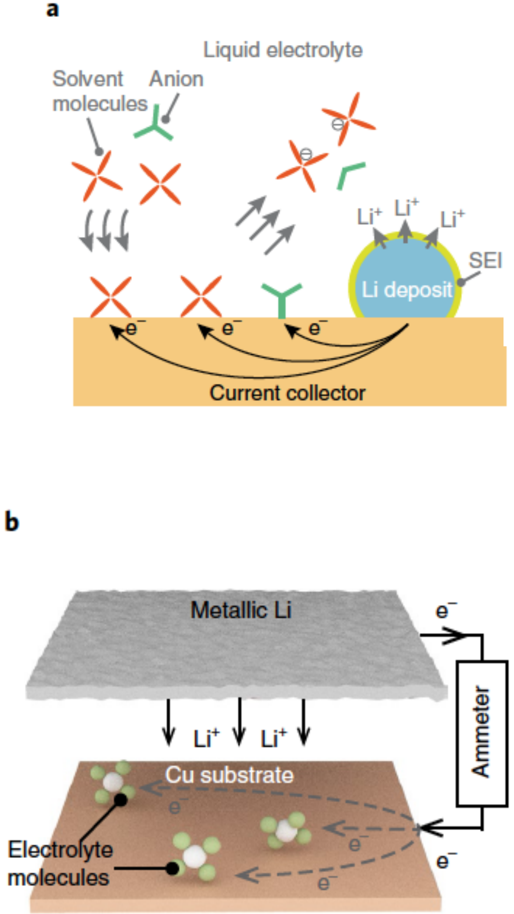
Technical Accomplishments and Progress

Discovery of Galvanic corrosion of Li metal involving a Kirkendall-type mechanism

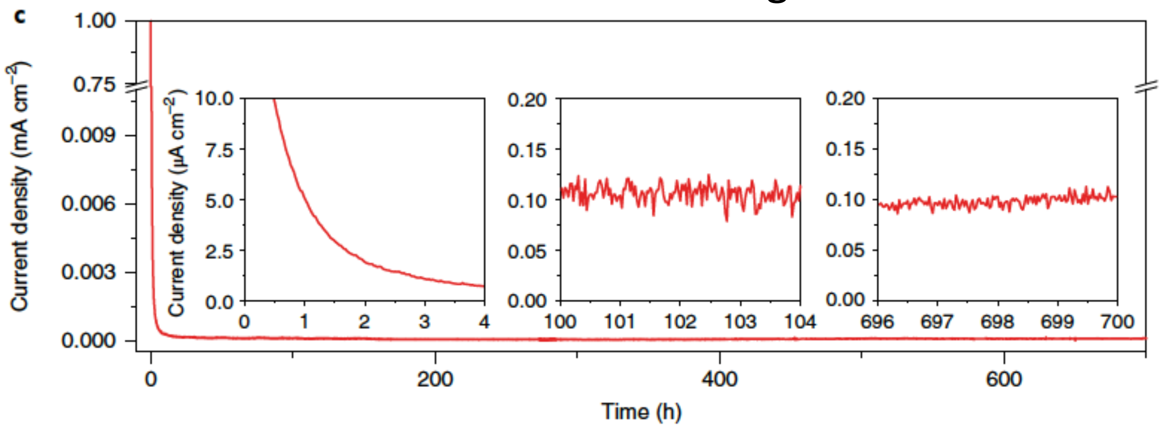
DOL/DME , 1M LiTFSI, 2% LiNO3

0hr 100hr 200hr

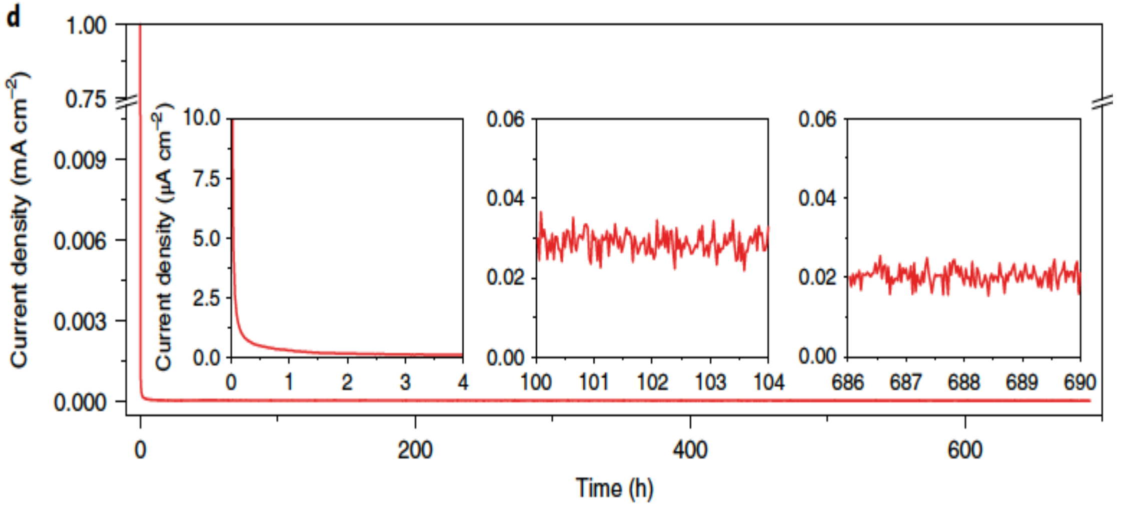




Cu foil without LiF coating



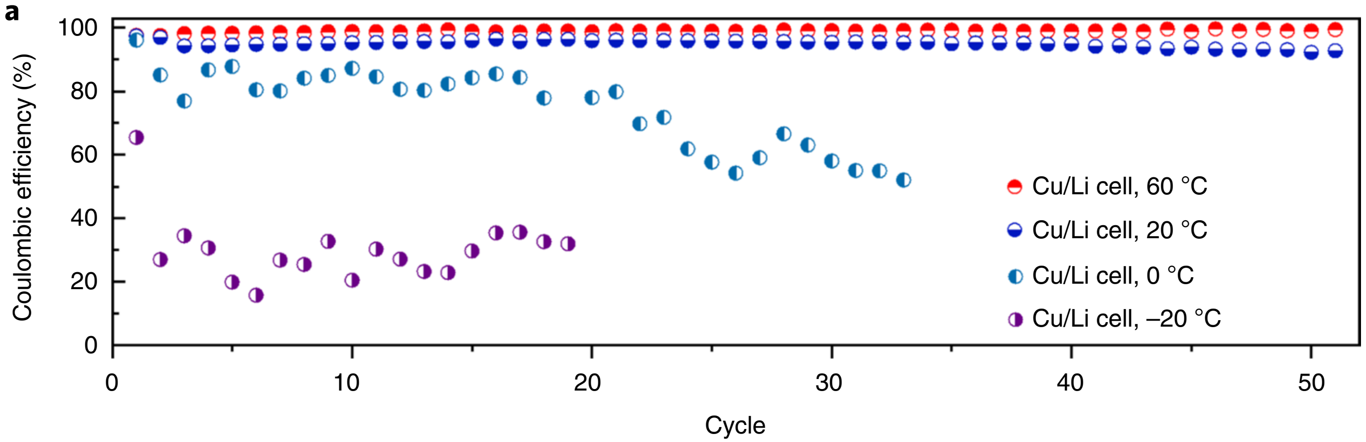
Cu foil with LiF coating

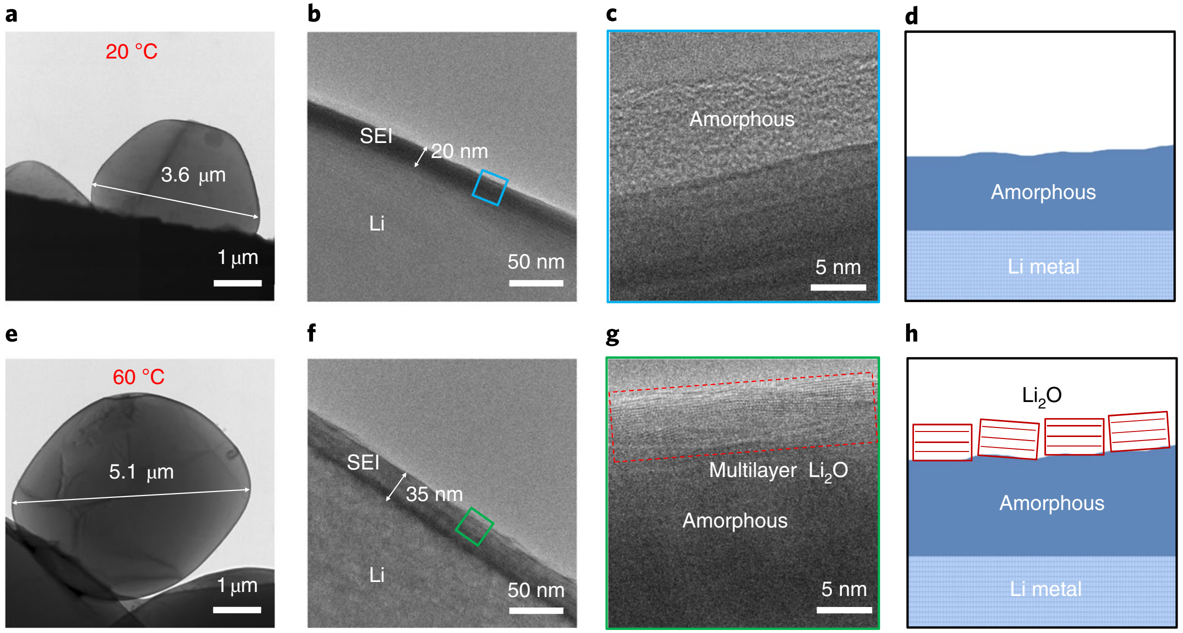


Dingchang Lin, Yayuan Liu, Nature Chemistry 11, 382–389, 2019

Technical Accomplishments and Progress

Temperature Dependence of SEI Structure and Coulombic Efficiency





DOL/DME/LiNO3 electrolyte

BATTERY500 CONSORTIUM

Jiangyan Wang, William Huang, Allen Pei, Yi Cui Nature Energy 4, 664–670, 2019

Responses to Previous Year Reviewers' Comments

None.

Collaboration and Coordination

Battery 500 PI's:
Jun Liu
Jie Xiao
Jason Zhang
Wu Xu

SLAC/ Stanford University:
Prof. Zhenan Bao
Prof. Mike Toney
Prof. William Chueh
Prof. Reiner Dauskardt
Prof. Steven Chu
Prof. Jian Qin
Prof. Wah Chiu
Prof. Robert Sinclair
Prof. Paul McIntyre

Remaining Challenges and Barriers

- It is challenging to generate Li metal with high coulombic efficiency and long cycle life to meet the Battery500 goal
- The best electrolyte and SEI structure are yet to be determined.

Proposed Future Work

- To further develop approaches for 3D Li metal anodes with stable interfacial modification, nearly zero-volume change both globally and locally.
- To develop electrolytes to form stable SEI assisted by cryoEM study.
- To develop polymer coating layer to facilitate the formation of stable SEI.

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high capacity Li metal anodes and the full battery cells to enable high energy lithium metal-based batteries to power electric vehicles, highly relevant to the VT Program goal.

- **Approach/Strategy:** This project combines advanced nanomaterials design, synthesis, characterization, battery assembly and testing, and guided by cryogenic electron microscopy study.

- **Technical Accomplishments and Progress:** This project has produced many significant results, meeting milestones. They include identifying the key issues in lithium metal batteries, using rational materials design, synthesis, characterization and simulation. The results have been published in top peer-reviewed scientific journals. The PI has received numerous invitations to speak in national and international conferences.

- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.

- **Proposed Future Work:** Rational future plan has been proposed.